REPLY

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We welcome the opportunity to address additional comments on our hypothesis for the origin of Neoproterozoic postglacial cap carbonates and their isotopic excursions.

Response to R.S. Shapiro. Shapiro (2002) summarizes field, petrographic, and geochemical criteria for the recognition of ancient hydrocarbon seep deposits, and suggests that we have insufficient evidence to link the deposition of cap carbonates with the destabilization of permafrost gas hydrate (Kennedy et al., 2001).

According to our hypothesis, destabilization of gas hydrate was not ''catastrophic,'' and it did not involve the ''entire seabed.'' Indeed, the seabed itself was disrupted only in the vicinity of inferred seeps. Methane was released over thousands of years from gas hydrate as a result of late glacial transgression and warming of the sediment surface. Permafrost gas hydrate is stable only at depths in excess of 150 m, and it would have responded slowly to changes in surface temperature. The source of the excess alkalinity required for carbonate precipitation needs to be distinguished from the location of precipitation and the manner in which the carbonate was deposited. Field data suggest that seeps were local features, in some cases associated with buried faults in the manner described by Shapiro.

We infer that alkalinity was produced near the seafloor at seeps as a result of the oxidation of methane by a consortium of methanotrophs using sulfate as an electron acceptor. Cap carbonates are nevertheless laterally persistent sheets because the bulk of the carbonate was precipitated in a marine environment, most likely at the chemocline. The common presence of mechanical laminae, cross-laminae, subtle scoured surfaces and textural grading, along with paleocurrent measurements, shows that much of the sediment was deposited from low-concentration turbidity currents.

Order of magnitude estimates for the amount of methane required to account for the −5‰ carbon isotope excursions observed in cap carbonates compare favorably with estimates of the mass of cap carbonate deposited at any particular stratigraphic level. We suspect that the apparent absence of expected isotopic heterogeneity in the vicinity of inferred seeps may be due in part to the lack of a concerted effort to acquire such data, and in part to the mineralogical and geochemical homogenization of these ancient rocks at most locations. Ongoing studies of isotopic variation in mm-thick fringing cements within cap carbonates in eastern California reveal $\delta^{13}C$ variations as great as 9‰.

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Our estimate for the amount of methane that might have been stored in permafrost gas hydrate (≥100 times the present inventory) was obtained from a consideration of the area of subaerially exposed shelves and intracratonic basins on an Earth sufficiently cold for continental ice sheets to develop at low latitude (<10°). The ultimate source of methane would have been buried organic matter. To our knowledge, there are no conflicts introduced by our hypothesis with respect to existing tectonic models or the Precambrian biosphere.

The anomalous cap facies, inferred in our paper to indicate potential pathways for hydrate-derived methane, do include many of the features described by Shapiro (Kennedy, 1996; Kennedy et al., 2001): peloidal and microbial textures, breccia-filled cavities lined by isopachous and botryoidal cements, and meter-scale seafloor relief. Additional evidence for gas release includes the presence of tubes, sheet cracks, and ''gas blisters.'' Fossil remains (annelids and molluscs) are not expected in Neoproterozoic examples, and the tubes in cap carbonates are not related to such organisms. The larger scale of some formerly aragonite and barite seafloor fans in cap carbonates compared with modern interstitial cement fans is not of concern to us.

In contrast to seeps linked to hydrocarbon systems, such as those of the Gulf of Mexico, methane seeps related to the destabilization of permafrost gas hydrate are not expected to be associated with bitumen because there is no reason for bitumen to have been produced. Moreover, most cap carbonates passed through the oil window long ago, and contain only indirect evidence for the former presence of hydrocarbons.

Response to M.D. Max and W.P. Dillon. Max and Dillon (2002) suggest that methane may have been released also during times of ice-sheet growth, eustatic lowering, and destabilization of oceanic gas hydrate through pressure release. We do not disagree with much of what they write, but we doubt that the scenario they describe applies to cap carbonates. Cap carbonates developed during the late stages of deglaciation. They are associated almost exclusively with the termination of major ice ages, and not with glacial-interglacial cycles. Available evidence suggests that they represent time scales that are inconsistent with catastrophic methane release (Kennedy and Christie-Blick, 1998).

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